PB-216 701

ANALYTICAL CHEMISTRY IN AIR POLLUTION

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The literature of air pollution has proliferated in recent years at a rate even greater than the growth of scientific literature as a whole. A good portion of this has been concerned, directly or indirectly, with new techniques of sample collection and analysis. It is not proposed here to review this mass of printed matter, but rather to discuss the state of the art generally, and to point out both some weak points and some hopeful signs. This pointing of the pen by a newcomer of recent, albeit intensive, exposure to these problems has some advantage. Long acceptance has not yet obscured the fact that some assumptions are merely assumptions, and no more, and that some authorities of the past are of the past. From this vantage point, then, these remarks are put forward in the hope that they may stimulate discussion, disagreement, and perhaps action.

It has been said that the scientific study of air pollution is in its infancy. This is a comforting thought, since it implies many irresponsible years ahead. It is more accurate, however, to say that the field is adolescent. It must soon cease to depend on foster parents such as industrial hygiene and combustion engineering, and become self-supporting.

Nearly all of the unresolved problems of the air analyst appear

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to boil down to two fundamental problems:

(1) What is to be analyzed and with what degree of certainty:

(2) What is the relationship between the sample, as presented to the analyst, and the atmosphere sampled?

These are always basic problems of the analytical chemist, but for the air analyst at this time, they have a particularly strong significance: In the current state of affairs, great uncertainty exists on both counts.

What should the air pollution chemist measure? The obvious answer is, "air pollution." However, a little reflection will reveal that "air pollution" is an abstraction, and is of itself incapable of measurement. Air pollutants, however, can be measured, provided we know what they are and can devise or adapt methods to measure them.

Thus while we cannot measure air pollution, we can measure certain of its attributes. Even this can be difficult. One of the most frequently studied classes of pollutants is particulate matter. Putting aside chemistry for the moment, let us consider the problem of determining the size of a particle and again ask our question, "What should we measure?" Are we interested in its geometric size, the dimensions of the particle as seen in a microscope? Are we interested in its Stokes diameter, the diameter of a sphere having the same settling velocity? Or is our concern with some measure of its light-scattering power, or some other derived function of constitution, form, and dimensions? The answer depends entirely upon the use to which the information is to be put. If air cleaning by impaction is being studied, the Stokes diameter is the most meaningful. If sieving is under examination, the

size of the smallest possible projection of the particle in two dimensions should be used.

The chemical study of pollutants is little simpler. For example, the measurement of sulfur dioxide concentration appears relatively simple, but once again the measure to be used must be determined by the needs of the situation. If a general index of air pollutant concentration is desired, to compare, say, hourly trends, the Autometer (Thomas and Ivie, 1952) or any other technique based upon conductivity (e.g., Wilson, 1954, anon., 1956) is adequate. On the other hand, if it is desired to measure sulfur dioxide specifically, a more selective method, such as that of West and Gaeke (1956) must be employed. But what of the sampling procedure? Once again, the purpose of the measurement must be considered. Are we investigating an odor complaint? This is quite likely to be caused by exposures of high intensity and short duration; hence a very rapid sample must be taken, since the long-term mean level may be quite low. Or is our interest in yearly trends? Here very long sampling periods are called for (Wanta and Stern, 1957).

Thus we see that the techniques to be used depend basically on the purpose of the measurement, which is not itself a chemical problem. The choice of technique must be based on a variety of information, including previous findings, both chemical and toxicological, as well as on legal definitions and standards, as well as on a certain "feel" for the situation.

Note that the first listed item of information is "previous chemical findings." This, in some measure, returns the responsibility for the correct selection of substance for analysis and of analytical

technique to the chemist. Even the toxicologist cannot furnish information on unidentified compounds. These chemical findings must result from two types of activity, neither of which receives the attention really due it: qualitative analysis, and analytical methods research. Under ideal conditions, the first step of any air pollution study should be a qualitative examination, in order to define the nature of the pollution. Failing this, such investigations can at least be conducted simultaneously with the routine monitoring program which appears to be the present standard technique.

Analytical methods research is severely needed in air pollution. Too many of our techniques have been brought over unmodified from industrial hygiene and toxicology practice, where the substance tested for is commonly present in relatively high concentrations, and where few interfering compounds need be considered. This is not to say that these methods may not be adequate in air pollution; it has, however, never been demonstrated that they <u>are</u> adequate. Rigorous evaluation of all our standard analytical techniques is needed; where these are shown to fail, new methods must be devised.

The other fundamental question is that of the relationship of the sample to the thing sampled. It seems at times that something akin to Heisenberg's uncertainty principle is at work here; we cannot analyze air pollutants without concentrating them, but the act of concentrating changes the sample. In fact, not a single collecting device exists, whether for gaseous or particulate pollutants, which has been demonstrated conclusively not to alter the material collected. In fact, it may be said with considerable justice that only recently

(e.g., Schadt and Cadle, 1957) have data been available on the collection efficiencies of many widely used devices. A complete demonstration of the effect of sampling on the sample is a formidable task, since it involves a complete reproduction of the natural environment under controlled conditions, with all concentrations known. This cannot be done until the effect of sampling upon the sample is known. The process is completely circular; therefore, it cannot be approached directly, but only by successive approximations.

There are two possible approaches. The first is by a study of the effects of sampling upon simplified models of gradually increasing complexity. Thus one may investigate first the sampling of a pure compound, then a binary mixture, etc. The best devices evolved may then be used to sample the free atmosphere, and the resulting findings employed to make the model more accurate. This cycle, if repeated sufficiently, should lead to an accurate knowledge of both polluted atmospheres and sampling systems. This approach has been in part utilized, for example, in a Public Health Service contract at Franklin Institute, under which collection of gases by compression is being studied.

A second approach involves analysis without sampling, using such methods as long path infrared (Stephens, et al., 1956) or ultraviolet (Renzetti, 1956) absorption. While the basic idea of direct analysis of the free atmosphere is extremely attractive, there are still too many substances which cannot be determined by these techniques in the concentrations in which they occur. Thus only a portion of the problem may be attacked in this way.

Another initially attractive approach is low temperature

condensation. However, although it appears possible to "freeze" reacting atmospheres at liquid oxygen temperatures, which are the lowest practical sampling temperatures, certain components cannot be removed quantitatively in this way. Also, it is usually necessary to rewarm the sample before analysis, whereupon reactions recommence, more rapidly than before because of the higher concentrations.

One idea which has been studied far too little is the possibility of "freezing" certain species chemically, by formation of a characteristic but unreactive compound. For example, it appears that the disulfitomercurate (II) ion formed in the West and Gaeke method for sulfur dioxide is very stable to oxidation. It is also characteristic, since only sulfur dioxide of all species to be expected in the atmosphere, yields this ion. In the field of particulate analysis, the impregnated gelatine technique as used by Crozier and Seely (1950), Seely (1952, 1955), Fidele and Vittori (1953), Vittori (1954, 1956), Farlow (1954, 1957), and Lodge and Panzoi (1954) has this potential, although the technique has so far been applied only to inorganic compounds of relatively stable types.

Recent work on the effect of aerosols on the toxicity of gases (LaBelle, et al., 1955) has re-emphasized the importance of the relation of chemical composition to particle size in aerosols, and of the study of sorbed vapors on them. Standard analytical methods yield no information on the former point, and very little on the latter. Both can be determined in many cases by the previously mentioned gelatine methods, or related techniques. The chemical "freeze" holds the sorbed materials, and the quantity can be inferred from the size of the reaction area.

If the supporting particulate matter is insoluble, its size may also be determined by inspection under the microscope. Specific reactions, either on gelatine, on membrane filters (Lodge, 1954) or on other suitable substrates (Lodge and Tufts, 1956) can give general information on the size spectrum of many species. Other microscopic techniques, including standard crystallographic methods (e.g., West, 1954), dispersion staining (Crossmon, 1956), and phase contrast microscopy (Schmidt) may be used for some insoluble compounds. Micrurgy probably represents the ultimate in elegance in this area.

Although these microscopic methods are extremely powerful, they require a type of skill not always available in the analytical laboratory. Junge (1953, 1954) has shown clearly that, given sufficiently sensitive analytical methods, similar information concerning the relationship of size to composition can be obtained from cascade impactor slides. Goetz (1957) has developed a "Particle Size Spectrometer" which gives a direct distribution of sizes on a suitable support. Particles are subjected to less violent treatment than in the impactor, and hence less deaggregation is to be expected. Analysis of different portions of the distribution yields information on the size spectra of the different species. Even simple sedimentation of aerosols resuspended in a liquid can give information, as in the recent work on lead from auto exhaust (Hirschler, et al., 1957). It must be assumed here that aggregation and deaggregation are negligible, and that the liquid has no effect on particle size. Since solubility increases at small sizes, the latter assumption is not without its dangers. Furthermore, the previous discussion of the numerous meanings of "particle size" should

be kept in mind here.

In summary, it has been pointed out that the purpose of a measurement must determine the techniques used in making that measurement. The knowledge necessary for an intelligent decision arises in part from previous analytical and other research. The nature and complexity of the sampling problem has been explored, and some work presently underway has been cited which may afford an eventual solution to this problem.

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